Ag/SiO$_2$: a novel catalyst with high activity and selectivity for hydrogenation of chloronitrobenzenes†

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Ag/SiO$_2$ prepared by an *in situ* reduction method are found, for the first time, to be highly effective and recyclable catalysts for the selective hydrogenation of a range of chloronitrobenzes to their corresponding chloroanilines, which are of great potential as industrially viable and cheap novel catalysts for the production of chloroanilines.

Chloroanilines (CAN), important intermediates for fine chemicals such as agrochemicals, pharmaceuticals and dyestuffs, are mainly produced by selective hydrogenation of the corresponding chloronitrobenzenes (CNB) over metal catalysts which include metallic Pt, Pd and Ru supported on active carbon, polymers and metal oxides, and Raney-Ni catalysts.[1–12] For most catalysts used right now that have high catalytic activity in the CNB hydrogenation reactions, a common drawback is the side reaction of catalytic hydrodechlorination of CNB over the metal catalysts. To solve the problem, several strategies have been developed, which include (1) alloying Pt with other metals[6] and the modification of Pt particles with sub-oxide species,[7] or with metal cations;[8] (2) using the synergic effect of bimetallic Pd–Ru catalysts[9] or (3) adding other reagents, such as NaOAc, pyridine, quinoline, to suppress the dechlorination reaction over Raney-Ni catalysts.[10] However, for Pd, Pt, Ni catalysts, the side reaction of hydrodechlorination still cannot be avoided completely. In the case of Ru-based catalysts, although high selectivity can be obtained, in most cases, it is still hard to convert 100% of the substrates into the target products except when choosing suitable supports such as SnO$_2$[11] or Fe$_2$O$_3$.[12]

Supported silver catalysts have long been extensively studied as oxidizing catalysts and have been applied industrially to the epoxidation of ethylene.[13,14] However, the catalytic reduction properties of silver have not drawn much attention, especially its potential as a catalyst for the catalytic reduction of fine chemicals. So far, only Nagase *et al.* have reported the selective hydrogenation of unsaturated aldehydes to the corresponding alcohols over silver catalysts supported on metal oxides,[15] showing that the activity and selectivity were only moderate. Since metal nanoparticles have many extraordinary properties that bulky metals do not have, the unique catalytic properties of nano-metal catalysts have been extensively explored. In this paper, we report an Ag/SiO$_2$ catalyst, prepared by a novel synthetic method, exhibiting unprecedented catalytic activity and selectivity for the hydrogenation of CNBs to the corresponding CANs. To the best of our knowledge, this is the first report on the catalytic properties of a supported silver catalyst for the selective hydrogenation of chloronitrobenzenes.

The Ag/SiO$_2$ catalysts were prepared by a new *in-situ* reduction method as shown in Scheme 1. The details of the preparation process can be found in the ESI.† Fig. 1A shows a typical TEM image of a fresh Ag/SiO$_2$ catalyst, from which it can be seen that the silver nanoparticles have an average size 7.0–9.0 nm and are highly dispersed on the silica support. Fig. 1B shows the XRD patterns of the fresh Ag/SiO$_2$ catalyst and two other silver catalysts. For the fresh Ag/SiO$_2$ catalyst (graph a), besides a peak of amorphous silica, no other peaks are present, implying that the silver particles are in a nano regime. In addition, the UV-vis spectrum (not shown here) of the fresh Ag/SiO$_2$ catalyst shows mainly one peak around 393 nm, which can be attributed to metallic silver, confirming that the silver cations are reduced in the preparation step.

$$\text{TEOS + APTES} \longrightarrow \text{NH}_2\text{-SiO}_2 \xrightarrow{\text{HCHO}} \text{CH}_2\text{O-SiO}_2$$

$$\xrightarrow{\text{AgNO}_3} \text{Ag/SiO}_2$$

Scheme 1 The preparation process for Ag/SiO$_2$ (TEOS = tetraethoxylsilicate, APTES = aminopropyltriethoxysilane).

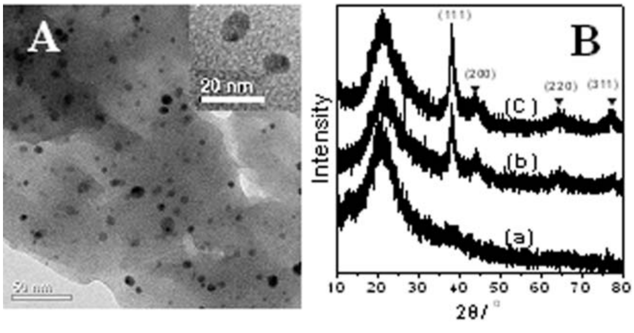

Fig. 1 (A) TEM picture of a fresh Ag/SiO$_2$ catalyst; (B) XRD patterns of Ag/SiO$_2$: (a) fresh catalyst dried at 120 °C; (b) recovered catalyst of (a); (c) fresh catalyst treated at 300 °C in H$_2$ for 2 h.

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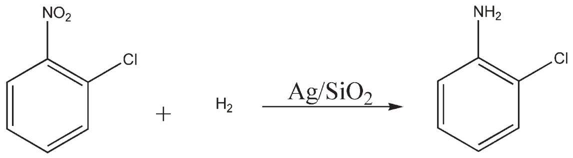
The hydrogenation of *o*-chloronitrobenzene (o-CNB) was employed as a probe reaction to test the activity and selectivity of the Ag/SiO_2 catalysts (Scheme 2) and the results are summarized in Table 1. At the initial reaction pressure of 0.5 MPa, the conversion of o-CNB was only 20% (entry 1). Increasing the reaction pressure to 2.0 MPa, the o-CNB conversion increased to 100% dramatically (entry 2), at the same time, the product selectivity to *o*-chloroaniline reached 100%, indicating that Ag/SiO_2 is a good catalyst for selective hydrogenation of o-CNB to *o*-chloroaniline. Further increasing the reaction pressure to 4.0 MPa, no changes in conversion or selectivity were observed (entry 3). When the reaction temperature was decreased from 140 °C to 100 °C, the conversion of o-CNB decreased to 35.9% with the selectivity of the target product (*o*-chloroaniline) being 80.7%, meanwhile, nitrobenzene, a dechlorinated byproduct, was formed (entry 4). It can be interpreted that the hydrogenation of the nitro group and hydrogenolysis of the C–Cl bond are competitive reactions at 100 °C, however, the hydrogenation of the nitro group is more sensitive to temperature, thus it is mostly accelerated at 140 °C and the selectivity to *o*-chloroaniline is improved significantly. The study on the influence of reaction time showed that the conversion could reach 100% in 1.5 h (entry 5). The recycled Ag/SiO_2 catalyst showed that the conversion of o-CNB decreased to 56.3% (entry 6). Further experiments proved that the organic fragments were not removed from the particle interface in the reaction process, and a small amount of H_2O had no influence on the activity of the Ag/SiO_2 catalyst, thus the reasons for the lost activity of the recycled Ag/SiO_2 catalyst must be related to other factors. The first possible reason is the aggregation of the silver particles: the TEM study (TEM image not shown here) of a recovered catalyst shows that the silver particles with a size of *ca.* 15.0–17.0 nm are bigger in contrast to a fresh catalyst. In addition, the XRD study shows that in the case of the recovered catalyst (graph b in Fig. 1B), the (111), (200), (220) and (311) diffraction lines of metallic silver are present, confirming that aggregation of silver particles took place during the reaction process. It is known that the particle size of the catalysts has a great influence on the catalyst activity;[16] we believe that the silver particle size plays a key role in the CNB hydrogenation catalyzed by silver. Another possible reason is the leaching of silver particles from the support. This assumption could be proved by the fact that 7.7% conversion of o-CNB was obtained (entry 7) when the reaction solution (catalyst was filtered out after one cycle) with an additional equivalent of substrate underwent the same procedure under the same conditions, indicating some leached sliver nanoparticles were present in the reaction solution. It should also be noted that the selectivity in this case dropped to 94.5%, implying that the support made a contribution to the improvement in the selectivity of the desired product. Pure CH_2O–SiO_2 was also tested and no hydrogenation reactions were observed (entry 8), which clearly proves that silver particles are the active component in the o-CNB hydrogenation reaction. For comparison, an Ag/SBA-15-imp catalyst with the size of the silver nanoparticles similar to the Ag/SiO_2 catalysts, prepared by the traditional wetness impregnation method, was also tested under identical hydrogenation conditions, showing only 40.3% of the o-CNB was converted (entry 9).



Scheme 2 Selective hydrogenation of *o*-chloronitrobenzene over Ag/SiO_2 catalyst to *o*-chloroaniline.

Table 1 Selective hydrogenation of *o*-chloronitrobenzene over fresh Ag/SiO_2 catalyst (dried only at 120 °C; reaction conditions: 0.1 g of the catalyst, 0.5 g of the substrate and 25 mL of ethanol)

Entry	*t*/h	*T*/ °C	*P*/MPa	Conversion (%)	Selectivity (%)
1	3	140	0.5	20	100
2	3	140	2.0	100	100
3	3	140	4.0	100	100
4	3	100	2.0	35.9	80.7[a]
5	1.5	140	2.0	100	100
6[b]	3	140	2.0	56.3	100
7[c]	3	140	2.0	7.7	94.5[a]
8[d]	3	140	2.0	0	0
9[e]	3	140	2.0	40.3	100
10[f]	3	140	2.0	15.3	100

[a] Nitrobenzene is a byproduct. [b] Recovered catalyst after the 1st reaction cycle (after entry 2). [c] Catalyst was filtered off after the reaction (entry 2) and the substrate was added for the second reaction cycle. [d] Reaction performed over CH_2O–SiO_2. [e] Ag/SBA-15-imp catalyst prepared by a wetness impregnation method. [f] Ag/SiO_2 catalyst treated at 300 °C in H_2 for 2 h.

In order to improve the stability of the silver nanoparticles on the support, after some trial-and-error experiments, we developed a simple method for the pretreatment of Ag/SiO_2 to enhance the interaction between the support and the silver nanoparticles. It has been found that after treating the Ag/SiO_2 at 300 °C in H_2 for 2 h, the leaching of silver particles can be avoided, though the conversion of o-CNB suffered and dropped to 15.3% under the same reaction conditions as used for fresh Ag/SiO_2 (entry 10 in Table 1). Furthermore, the XRD pattern of the heat-treated catalyst showed that the silver particles were bigger in comparison to the fresh catalyst, as can be seen in graph c of Fig. 1B, the intensity of the characteristic diffraction lines (111), (200), (220) and (311) of metallic silver becomes more significant. However, when the treatment temperature was further decreased to 200 °C (denoted as Ag/SiO_2-200), the TEM and XRD studies showed little change in the silver nanoparticles in comparison to the fresh catalyst, but in this case the catalytic hydrogenation of o-CNB over Ag/SiO_2-200 catalyst showed that the high activity and selectivity were maintained. More tests show that the recovered catalyst (Ag/SiO_2-200) could be used repeatedly for consecutive reactions, and no significant loss in catalytic efficiency was found (as shown in the ESI†), implying that the leaching of silver particles was effectively avoided.

Following the catalytic hydrogenation of o-CNB presented above, the hydrogenations of other CNBs over the Ag/SiO_2-200 catalyst were also conducted, of which the detailed results are shown in the ESI.† When nitrobenzene was used as a substrate, the conversion was 93.9% and aniline was the only product. The reason for the fact that the byproduct of hydrogenation of o-CNB is nitrobenzene instead of aniline may be because the reduction rate of nitrobenzene is slower than that of o-CNB. The Ag/SiO_2-200 catalyst also showed high activity and selectivity for dichloro-containing nitrobenzenes, *e.g.* 2,5-dichloronitrobenzene and 3,4-dichloronitrobenzene. It is surprising to note that the side reactions of hydrodechlorination were completely avoided for these chloro-containing nitrobenzenes. In addition, two substrates with electrodonating groups, *p*-nitrotoluene and *o*-nitrophenol, were also effectively reduced over the Ag/SiO$_2$-200 catalyst.

In conclusion, we have reported an Ag/SiO$_2$-200 catalyst prepared by a new synthetic method, which shows a very good activity and selectivity for hydrogenation of chloronitrobenzenes to the corresponding chloroanilines. The size of the silver nanoparticles as well as the interaction between the silver nanoparticles and the silica support may play an important role in the catalytic reaction system. The results presented here highlight the great potential of Ag/SiO$_2$ catalysts in the selective hydrogenation of chloronitrobenzenes on a large scale. Further optimization of the preparation process and catalytic activity of the Ag/SiO$_2$ catalyst are currently in progress.

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